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(54) Negative Electrode [Anode] for Alkaline Battery

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(57) Scope of Patent Claim

1. A negative electrode [anode] for an alkaline battery, characterized in that a zinc dispersion containing 99 to 60 wt% zinc, 1 to 40 wt% of at least one of the following elements: bismuth, lead, thallium, cadmium, tin, indium, antimony, selenium, and tellurium or oxides of these metals, and an aqueous polyvinyl alcohol solution containing boric acid or at least one compound that releases boric acid ions in an aqueous alkaline solution is housed in an ion-permeable vessel and is used after being brought into contact with an alkaline solution.

Detailed Description of the Invention

The present invention pertains to an alkaline battery that uses zinc as the negative electrode [anode] active substance and in particular, relates to an alkaline battery with improved shelf life and whose cycle life is prolonged with repeated charging and discharging.

Primary and secondary batteries that use zinc as the anode active substance are made from inexpensive starting materials and have a high voltage and high discharge current. Those that use an alkaline electrolyte are particularly excellent in terms of low-temperature properties and heavy-load properties. For instance, the following characteristics have already been realized with this type of primary or secondary battery: (1) Good discharge properties and low-temperature properties are obtained by dispersing zinc in powder form, particle form, or fiber form in a gel of an aqueous solution of carboxymethylcellulose to make a zinc anode. (2) The effective surface area of the zinc is increased by dispersing the above-mentioned gel in the pores of the

porous zinc to make a zinc anode. (3) Zinc is amalgamated with 3 to 10 wt% mercury with 97 to 90 wt% zinc in order to inhibit undesirable hydrogen generation due to contact with electrolyte from places where the zinc in powder, particle, or fiber form covers a large surface area. (4) The effect of inhibiting hydrogen generation is further increased by mixing less than 0.3 wt% of a metal that tends to amalgamate, such as cadmium, thallium, tin, bismuth, lead, or tellurium, with the mercury during amalgamation so that these metals uniformly precipitate in the zinc. (5) Dendrite formation, which causes internal short-circuiting of secondary batteries, is prevented by adding a small amount of ions of a metal that tends to amalgamate, such as Bi^{3+} , Ti^+ , Ti^{3+} , Cd^{2+} , Sn^{2+} , Sn^{4+} , Pb^{2+} , As^{3+} , As^{5+} , and the like, or hydroxy or oxy complexes of these metals, to the electrolyte solution so that these metals, will precipitate on the zinc surface. Similarly, in order to prevent dendrite formation, (6) a sulfur compound is added to the electrolyte solution or (7) the amount of alkaline electrolyte is brought to a very small amount in comparison to the amount of zinc in order to prevent the production of acidic zinc ions, and the like. However, each of these methods has its own disadvantages. For instance, with method (1) there is an increase in the use of mercury to prevent generation of hydrogen from places where this generation of hydrogen is increased. Therefore, product costs are increased and countermeasures against toxicity are needed for manufacture. Moreover, syneresis and flocculation occur with long-term or high-temperature storage and the zinc particles separate from the gel and aggregate. Therefore, contact with the collector degrades and there is a reduction in the zinc utilization factor with high-current discharge. There is a reduction in current efficiency and hydrogen is generated and there is a reduction in charge capacity and

battery capacity because of the zinc oxide that precipitates after discharge around the collector ring in the case of secondary batteries in particular. As with method (1), gradual syneresis of the gel with separation from the pores of the porous zinc takes place with the method in (2) and this leads to insufficient electrolyte for discharge and a reduction in the zinc utilization factor, making it impossible to store the battery. In addition, the effect of increased effective surface area of the porous zinc is realized with low-current discharge, but is not realized with very fast discharge. That is, deactivation rapidly proceeds from the outside surface in places where current is focused only on the outside surface and use of the zinc on the inside is hindered. Charging does not penetrate to the inside and there is a reduction in the zinc utilization factor with secondary batteries in particular. Furthermore, the bonds between the zinc particles are broken by discharging, making it impossible for the anode to retain the initial shape. Moreover, in addition to the high cost of the mercury that is used in method (3), the surface is made smooth, making it difficult to retain porosity. Moreover, the liquid particles of mercury that are produced during discharging induce electrode deformation and internal short-circuiting. In the case of secondary batteries in particular, the liquid particles that are produced with discharging separate and aggregate outside the amalgam system, making it impossible to achieve a uniform amalgamation over the entire surface of the zinc metal that is gradually produced with charging. Thus, there is a further reduction in the desired inhibition of hydrogen generation. Moreover, method (4) does not improve on conventional methods to such an extent that there is a large reduction in the amount of mercury that is used, and because little metal is added to the mercury, no benefit is seen in terms of the zinc utilization factor or battery life. The

solubility of the metal ions that are added by method (5) is low at 10^{-3} M/liter and therefore, although effects are obtained with initial charging, there is a sudden reduction with the next charge cycle. These additional metal ions precipitate before the zinc with the first discharge and there are virtually no metal ions in the solution. In addition, the oxidation-reduction potential of the metal ions is more positive than that of zinc and therefore, they do not return to the form of the metal ion. Thus, these metal ions cannot precipitate on the zinc metal that has precipitated during the next charge cycle and they do not participate in the prevention of dendrite formation. Moreover, by means of the method in (6), the cathode active substance is oxidized and depleted because the sulfur compound lacks oxidation resistance and the effects therefore are not permanent. Moreover, there is a disadvantage with the method in (7) that the zinc utilization factor is low and heavy load properties are poor.

Consequently, results that are in line with the individual goals of these methods are realized, but overall they are not satisfactory methods because they are accompanied by other disadvantages.

The present invention is an anode for an alkaline battery, characterized in that a zinc dispersion containing 99 to 60 wt% zinc, 1 to 40 wt% of at least one of the following elements: bismuth, lead, thallium, cadmium, tin, indium, antimony, selenium, and tellurium or oxides of these metals, and an aqueous polyvinyl alcohol solution containing boric acid or at least one compound that releases boric acid ions in an aqueous alkaline solution is housed in an ion-permeable vessel and is used after being brought into contact with an alkaline solution.

The zinc here can be in powder, particle, or fiber form. The bismuth, lead, thallium, cadmium, tin, indium, antimony, selenium, tellurium, and oxides of these metals can be in powder, particle, fiber, or porous form, and the amount is 1 to 40 wt%, preferably 3 wt% or more. Consequently, in contrast to conventional use for prevention of hydrogen generation or self-discharge of the zinc, a large amount is used. Moreover, these substances can be mixed with the zinc, or a prealloy with the zinc is temporarily made and used. The aqueous polyvinyl alcohol solution that is used is an aqueous solution containing 0.3 to 20 mol% boric acid or a compound that will release boric acid ions in an aqueous alkaline solution and 99.7 to 70 mol% of polyvinyl alcohol. The mixture of these three components is obtained, for instance, by adding and uniformly mixing zinc and bismuth, and the like in the aqueous polyvinyl alcohol solution to make a zinc dispersion, or mixing the three in powder form and then adding water to make the same zinc dispersion, and then bringing this into contact with an aqueous solution of a hydroxide of an alkali metal or alkaline-earth metal, such as sodium hydroxide. The zinc dispersion becomes a molded gelled body that is easy to handle during this step.

This type of gel-like zinc dispersion that becomes a gelled body gradually changes to a porous metal unit during use as a battery electrode. Moreover, the above-mentioned bismuth, lead, thallium, cadmium, tin, indium, antimony, selenium, tellurium, and the like become the conductive base of this electrode. These metals become porous metals that precipitate by reacting with the metallic zinc according to $Zn + Mo \rightarrow ZnO + M$ when an oxide is used because their standard oxidation-reduction potential is more positive than that of zinc. Moreover, these metals will not oxidize and remain as metals, even when the zinc is oxidized by ZnO or $Zn(OH)_n^{2-n}$ ($0 \leq n \leq 4$) with discharge.

As a result, the conductive base, that is, the collector ring surface area, is always very large, and thus, hydrogen generation and dendrite formation do not occur.

The amount of this metal needed to support a porous metal body of bismuth and the like that is maintained on a very broad surface area and acts as a collector, taking into consideration the active substance, is 1 wt% or more, particularly 3 wt% or more, up to 40 wt%.

With respect to the polyvinyl alcohol containing boric acid or a compound that will release boric acid ions in an aqueous alkaline solution, the zinc dispersion is brought into contact with the alkaline solution and is then crosslinked with the boron. Moreover, elution of some of the zinc or acidic zinc ions as a result of charging-discharging is prevented and spreading to the cathode side is controlled. Moreover, the large amounts of ZnO that are produced during discharge are retained without ionizing. The gelled body that is obtained after bringing the zinc dispersion into contact with the alkaline solution has very good ion conductivity and the ability to prevent permeation of $Zn(OH)_n^{2-n}$, and this $Zn(OH)_n^{2-n}$ that has been produced as a result of discharge does not diffuse to the cathode side. Consequently, deterioration of battery life is prevented. Moreover, this gelled unit has elasticity and a tendency for the zinc and metal such as bismuth and the like to become compressed is prevented. Therefore, there is no reduction in discharge capacity during storage.

Examples of the present invention will now be described:

Ten parts of metallic bismuth were thoroughly mixed with 100 parts of 60-mesh zinc metal powder and then 70 parts of this and an aqueous solution containing 0.4 mol% boric acid and 5 mol% polyvinyl alcohol were thoroughly mixed. Then this was

introduced into a nylon nonwoven cylinder of 6 mm diameter with a base and a brass rod of 3-mm diameter was inserted into the middle as the conductor. This was immersed in an aqueous 35 wt% potassium hydroxide solution and set aside overnight. As a result, an elastic anode that retained its shape with crosslinked polyvinyl alcohol and was made into one unit with the diaphragm was obtained. A No. 3 battery was assembled using a molded article made from 85 parts of electrolytic manganese dioxide as the cathode active substance and 15 parts of graphite powder and the properties of the above-mentioned anode and of the battery were studied (battery A). Battery B was made as the Comparative Example under the same conditions, with the exception that the anode was constructed from a mixture of 100 parts of zinc metal powder and 35 weight [parts] of a gelled unit of aqueous potassium hydroxide solution containing 4 wt% carboxymethylcellulose. The properties of batteries A and B were investigated.

The batteries were stored in a thermostatic chamber at constant humidity at 45°C and 75% relative humidity and after a specific amount of time, they were removed from the chamber and discharged at 4 Ω and the capacity was determined. The results are shown in Table 1 in comparison to the initial capacity.

Table 1. (Percentage of retained capacity with initial capacity of 100%)

| | 0 days | 10 days | 30 days | 50 days | 100 days | 150 days | 200 days | 300 days |
|-----------|--------|---------|---------|---------|----------|----------|----------|----------|
| Battery A | 100% | 99 | 98.5 | 98 | 96 | 93.5 | 92.5 | 90.0 |
| Battery B | 100% | 97.5 | 96.5 | 95 | 92 | 90 | 88.5 | 83.5 |

It is therefore clear that shelf life is very much improved by the method of the present invention.

Heavy-load properties of the batteries obtained above were investigated. That is, when the short-circuit current of both batteries was determined, that of battery A was an average of 20.5 A and that of battery B was an average of 11.7 A, with a much larger current being obtained from battery A of the present invention. Moreover, when both batteries were submitted to 2Ω discharge tests, the capacity of battery A was 1.1 Ahr, while that of B was 0.8 Ahr. It was determined that battery A of the present invention was superior.

Example 2

The composition ratio of metallic bismuth in Example 1 was varied up to 50 wt% and at the same time, the amount of boric acid in the polyvinyl alcohol was varied from 0.1 mol% to 30 mol% and the shelf life and other properties were evaluated. The results are shown in Table 2.

Table 2.

Key: Wt% of bismuth in zinc/
Mol% of boric acid in polyvinyl alcohol

| 亜鉛中ビスマス の組成重量% | | 0.5 | 1.0 | 3.0 | 1.0 | 2.0 | 3.0 | 4.0 | 5.0 |
|----------------------------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| ポリビニ ールアルコ ル中のホー酸 のモル数% | | 0.5 | 1.0 | 3.0 | 1.0 | 2.0 | 3.0 | 4.0 | 5.0 |
| 0.1 | C s | 6 | 21 | 53 | 80 | 87 | 75 | 52 | 34 |
| | C h | 89 | 115 | 147 | 185 | 162 | 123 | 98 | 78 |
| 0.3 | C s | 4 | 35 | 62 | 98 | 93 | 85 | 65 | 47 |
| | C h | 100 | 143 | 169 | 201 | 284 | 131 | 101 | 99 |
| 1.0 | C s | 17 | 50 | 76 | 118 | 108 | 92 | 77 | 56 |
| | C h | 101 | 168 | 204 | 235 | 226 | 142 | 104 | 101 |
| 5 | C s | 24 | 75 | 82 | 125 | 122 | 97 | 80 | 62 |
| | C h | 92 | 172 | 243 | 274 | 262 | 129 | 112 | 100 |
| 10 | C s | 58 | 86 | 102 | 116 | 114 | 94 | 81 | 60 |
| | C h | 85 | 166 | 225 | 252 | 243 | 117 | 108 | 96 |
| 15 | C s | 97 | 97 | 103 | 107 | 102 | 88 | 75 | 53 |
| | C h | 78 | 131 | 174 | 211 | 187 | 109 | 99 | 92 |
| 20 | C s | 73 | 82 | 83 | 92 | 90 | 76 | 58 | 35 |
| | C h | 69 | 123 | 140 | 145 | 138 | 100 | 94 | 90 |
| 30 | C s | 45 | 60 | 62 | 65 | 60 | 45 | 32 | 21 |
| | C h | 65 | 74 | 86 | 102 | 101 | 96 | 87 | 65 |

The batteries were stored by being set aside for 250 days at 45°C and 70% humidity and then the capacity was determined with continuous discharge at 10 Ω. The initial capacity of battery B was set at 100 and the capacity on day 250 was B'. Moreover, the capacity on day 250 of battery A was A'. Cs (storage capacity) in Table 2 is $(A' - B')/(100 - B')$ represented in percent. Moreover, heavy load properties were investigated by conducting 2 Ω continuous discharge tests. In this case, Ch (heavy-

load capacity) is $(a - b)/b$ represented in percent. $C_s > 0$, $C_h > 100$ indicates that the results are good. As is clear from Table 2, good results are realized with the method of the present invention when the bismuth mixture ratio is 1 to 40 wt% and the molar ratio of boric acid in the polyvinyl alcohol is between 0.3 and 20%. Moreover, results were obtained as a result of conducting the same tests with thallium, tin, cadmium, zinc, indium, antimony, tellurium, and the like, in place of metallic bismuth. It was determined that good results are obtained when the mixture ratio of these metals is 40 mol% and the molar ratio of boric acid in the polyvinyl alcohol is within a range of 0.3 to 20%.

Example 3

When the same tests as in Examples 1 and 2 were conducted by uniformly mixing with the zinc oxides of these metals in place of the bismuth and the like to obtain the same weight percentage in terms of metal, it was shown that these oxides have the same effect as the metals. That is, it was confirmed that when these metal oxides are brought into contact with metallic zinc, a porous body of these metals forms through a reaction such as $3\text{Zn} + \text{M}_2\text{O}_3 \rightarrow 3\text{ZnO} + 2\text{M}$, and this acts as a metal collector.

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⑯アルカリ電池用陰極

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⑯特許請求の範囲

1 亜鉛9.9乃至60重量%と、ビスマス、鉛、タリウム、カドミウム、スズ、インジウム、アンチモン、セレン、テルル或いはこれ等金属の酸化物の少なくとも一種1乃至40重量%と、ホウ酸又はアルカリ水溶液中でホウ酸素酸イオンを放出する化合物の少なくとも一種を含有するポリビニルアルコール水溶液とを含む亜鉛分散体をイオン透過性容器に収容してアルカリ液に接触して後供することを特徴とするアルカリ電池用陰極。

発明の詳細な説明

この発明は亜鉛を陰極活性物質とするアルカリ電池に係り、特に重負荷特性、貯蔵特性を向上するとともに充放電繰返しサイクル寿命を延長するアルカリ電池に関するものである。

亜鉛を陰極活性物質として用いた一次又は二次電池は原料価額が低廉で電圧が高く放電電流が大であり、特に電解液をアルカリ性としたものは低温度特性、重負荷特性にすぐれるものである。例えばこの種の一次又は二次電池で既に行われている

ことは(1)粉末、粒子又は線状の亜鉛をカルボキシメチルセルローズの水溶液ゲル体に分散して亜鉛陰極とすることにより放電特性、低温特性を良好にする。(2)多孔性亜鉛体の孔中に前記ゲル体を分散して亜鉛陰極とすることにより亜鉛の有効表面積を大にする。(3)亜鉛を粉末、粒状又は多孔状の表面積大の状態で使用する所から電解質との接触による好ましくない水素発生を抑制するために亜鉛9.7重量%乃至9.0重量%に対し3重量%乃至5重量%の水銀により亜鉛をアマルガム化する。(4)アマルガム化する際に水銀中にカドミウム、タリウム、スズ、ビスマス、鉛、テルルのような易アマルガム化金属を0.3重量%以内混合しておくことにより亜鉛に均一にこれ等金属を析出させて10 10重量%の水銀により亜鉛をアマルガム化する。(5)電解質溶液中に易アマルガム化金属のイオン例えば B_{13}^{3+} , Tl^{+} , Tl^{3+} , Cd^{2+} , Sn^{2+} , Sn^{4+} , Pb^{2+} , As^{3+} , As^{5+} 等か又はこれ等金属イオンのヒドロキシ乃至はオキシ錯体を少量添加することにより液中からこれ等金属を亜鉛表面に析出させ二次電池での内部短絡障害を成すデンドライト生成を防止する。同様にデンドライト生成を防止するため(6)電解質溶液中に硫黄化合物を添加するか、或いは又(7)亜鉛酸イオンの生成を防止するため亜鉛の量に比較してアルカリ電解質を極端に少量にする等である。しかしこれ等の方法にもそれぞれ欠点が存在する。例えば(1)にあつては水素発生量が増大する所からこの発生を抑制する水銀の使用が増大する。このため製造費を高め、製造上毒性30への対策を要し、長期又は高温保存で離漿解膠を招き、ゲル液から亜鉛粒子が分離凝集するため素電子との接触を劣悪にし、大電流放電での亜鉛利用率が低下する。特に二次電池である場合集電子周囲に放電後析出する酸化亜鉛のため充電時に電流効率を減少し水素発生を惹起すると共に充電容量減少、電池容量低下を招来する。又(2)にあつては(1)の場合と同様に多孔性亜鉛体の孔中からゲル

液が次第に離漬するため、放電時に電解液が不足することになり、亜鉛利用率を低下し貯蔵に適しない。のみならず亜鉛を多孔性として有効表面積を大にした効果は低電流放電に得られて急速放電では得られない。即ち外部表面のみに電流が集中する所から不活性化は外部表面から急激に進行して内部の利用を妨げる。特に二次電池に於いては充電が内部に浸透せず亜鉛利用率を低下し、更に放電に伴い亜鉛粒子間の結合を崩壊して初期形状の維持が不可能になる。又(3)にあつては水銀が高価額である上、表面を平滑化して多孔性の維持を困難にし、放電時に生成する水銀の液粒が電極変形並びに内部短絡を招来する。特に二次電池である場合放電時に生成した液粒がアマルガム系外に分離凝集し充電時に次第に生成する亜鉛金属の表面全面の均質なアマルガム化を困難にして目的とした水素発生の抑制効果さえ低下するに到る。又(4)にあつては水銀使用量の大巾節減をみる程度の改良には達しないのみならず特に二次電池の場合水銀中での混合量が少いため亜鉛利用率及び電池寿命の点からの利点がない。又(5)にあつては添加する金属イオンの溶解度が 10^{-3} M/l 程度に小であるため最初の充電時に効果が得られても次回の充電から急速に減少するようになる。この添加金属イオンは最初の充電時に亜鉛に先んじて析出し溶液中の金属イオンを殆どなくしてしまう。そして酸化還元電位が亜鉛よりも正であるため金属イオンに戻ることがない。それ故次回充電に際して析出した亜鉛金属上に析出出来ずデンドライト生成抑制に寄与しなくなるのである。又(6)にあつては硫黄化合物の耐酸化性欠陥により陽極活物質に酸化消耗されて効果を永続的にしない。そして(7)にあつては亜鉛利用率が低く重負荷特性が悪い欠点がとゞめられている。

従つてこれ等の改良は個々の目的に沿う効果を得ていても他方で不都合の点を伴うために全体として満足されない。

この発明は亜鉛を陰極活物質とするアルカリ電池の陰極性能について、亜鉛極の利用率、貯蔵特性、充放電サイクル寿命の三点につき向上をはかつたものである。即ち亜鉛 99 乃至 60 重量%と、ビスマス、鉛、タリウム、カドミウム、スズ、インジウム、アンチモン、セレン、テルル或いはこれら等の金属の酸化物の少なくとも一種 1 乃至 40

重量%と、ホウ酸又はアルカリ水溶液中でホウ素酸素イオンを放出する化合物の少なくとも一種を含有するポリビニルアルコール水溶液とを含む亜鉛分散体をイオン透過性容器に収容してアルカリ液に接触して後供することを特徴とするアルカリ電池用陰極にある。

こゝで亜鉛は粉末状、粒状、線状であつてよい。ビスマス、鉛、タリウム、カドミウム、スズ、インジウム、アンチモン、セレン、テルル或いはこれら等の金属の酸化物は粉末状、粒状、線状、多孔状であつてよく、その量は 1 乃至 40 重量%好ましくは 3 重量%以上とする。従つて従来の水素発生や亜鉛の自己放電防止に使用した場合と異り使用量を大にしている。そして亜鉛に対し混合してよいが、時に亜鉛と予じめ合金を作成しておいて使用に供してもよろしい。併用されるポリビニルアルコール水溶液は、ホウ酸又はアルカリ水溶液中でホウ素酸素酸イオンを放出する化合物を 0.3 乃至 20 モル%とポリビニルアルコール 99.7 乃至 70 モル%とを含む水溶液であればよろしい。これ等三者の混合は例えばポリビニルアルコール水溶液中に亜鉛及びビスマス等の混合物を追加均一に混合して亜鉛分散体とするか又は三者とも粉末状態で混合して後注水し同様の亜鉛分散体とするかしてこれを苛性ソーダなどアルカリ金属乃至アルカリ土金属の水酸化物水溶液に接触させる。この段階で亜鉛分散体は取扱い容易に成型されたゲル体となる。

このようなゲル体をなすゲル状亜鉛分散体は電池電極として使用中次第に金属多孔体へと変化する。そしてその導電性基体をなすものは上述のビスマス、鉛、タリウム、カドミウム、スズ、インジウム、アンチモン、セレン、テルル等の金属である。これ等の金属は亜鉛よりもその標準酸化還元電位が正であるため酸化物を使用した場合にあっても金属亜鉛と反応し $Zn + M_0 \rightarrow ZnO + M$ のような反応により多孔性金属となつて析出することになる。そして亜鉛が放電によつて ZnO 乃至 $Zn(OH)_{2-n}$ ($0 \leq n \leq 4$) のように酸化されてもこれ等の金属は酸化されず金属としてとどまる。この結果導電性基体即ち集電子表面積は常にきわめて広く保たれることになり充電時の過電圧も極めて低く保たれる結果水素発生やデンドライト生成をみることがない。

このように集電体としての作用を有し極めて広い表面積に保たれた多孔性のビスマス等金属体を保持する必要上これ等金属の量は活物質を考慮して1%以上特に3重量%以上40重量%まで有効である。

ホウ酸又はアルカリ水溶液中にホウ素酸素酸イオンを放出する化合物を含有するポリビニルアルコールは亜鉛分散体がアルカリ液に接触した後ホウ素架橋される。そして充放電の結果溶出する一部亜鉛乃至亜鉛酸イオンを抑制して陽極側への拡散を制御すると共に放電時に多量生成する ZnO をイオン化しないで維持することに寄与する。亜鉛分散体のアルカリ液接触後に得られるゲル体はイオン伝導性が極めて良好であり且つ $Zn(OH)_2$ の通過を防ぐ性質を有して放電の結果生成した $Zn(OH)_2$ を陽極側に拡散させない。従つて電池寿命劣化を防止する。又このゲル体は弾性を持つて亜鉛並びにビスマス等金属が下方に偏積することを妨げるから貯蔵中の放電容量低下を招くこともない。

次にこの発明の実施例について述べる。

実施例 1

60メッシュ通過の亜鉛金属粉100部に金属※

表 1 (初期値を100%としての容量の相対比)

| | 0日 | 10日 | 30日 | 50日 | 100日 | 150 | 200日 | 300日 |
|------|------|------|------|-----|------|------|------|------|
| 電池 A | 100% | 99 | 98.5 | 98 | 96 | 93.5 | 92.5 | 90.0 |
| 電池 B | 100% | 97.5 | 96.5 | 95 | 92 | 90 | 88.5 | 83.5 |

このように、本発明の方法では貯蔵特性がいちじるしく改善されているのがわかる。

上記においてえられた電池につき、重負荷特性を調べた。すなわち、両者の電池につき短絡電流を測定したところ、電池Aでは平均2.05A電池Bでは平均1.17Aであり、本発明の電池Aの方がはるかに大電流をとり出せることがわかつた。また更に両者を20放電試験を行なつたところ、容量は電池Aが1.1Ahrであるのに対し、電池

※ビスマス10部をよく混合し、ついでこれの70部とホウ酸0.4モル%およびポリビニルアルコール5モル%を含む水溶液とをよく混合し、しかるのちこれを6mmのナイロン不織布底つき円筒の5中に入れ、中央に導電体として3mmのしんちゆう棒を挿入したのち、これを35重量%カセイカリ水溶液に浸漬して一昼夜放置すると極めて弾性ある架橋ポリビニルアルコールで形状を保ち、かつ隔膜と一体化された陰極体を作ることができる。10陽極活物質としては電解二酸化マンガン85部、黒鉛粉15部より成る成形体を用い上記陰極体を用いて単三型電池を組み立てその電池特性を調べた(Aとする。)比較例として亜鉛金属粉末100部と4重量%カルボキシメチルセルローズを含む1535重量カセイカリ水溶液ゲル体との混合物で陰極体を構成した他は上記と同じ条件で電池Bを製した。この電池AおよびBにつき種々の特性を調べた。

45℃, 75%相対湿度の恒温恒湿室内で貯蔵20し、所定時間後電池をとり出し40放電にかけて、その容量を調べこれを、初期値と比較した所表1に示す結果をえた。

30 Bは0.8Ahrであり、本発明の電池Aの方がすぐれていることが判つた。

実施例 2

実施例1において、金属ビスマスの組成比を50重量%まで間にてかえると同時に、ポリビニルアルコール中のホー酸を0.1モル%から30モル%までかえて、貯蔵特性その他特性の評価を行つた。結果を表2に示す。

表 2

| 亜鉛中ビスマスの組成重量% | | 0.5 | 1.0 | 3.0 | 10 | 20 | 30 | 40 | 50 |
|-----------------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| ポリビニールアルコール中のホー酸のモル数% | | | | | | | | | |
| 0.1 | C s | 0 | 21 | 53 | 80 | 87 | 75 | 52 | 34 |
| | C h | 89 | 115 | 147 | 185 | 162 | 123 | 98 | 78 |
| 0.3 | C s | 4 | 35 | 62 | 98 | 93 | 85 | 65 | 47 |
| | C h | 100 | 143 | 169 | 201 | 284 | 131 | 101 | 99 |
| 1.0 | C s | 17 | 50 | 76 | 118 | 108 | 92 | 77 | 56 |
| | C h | 101 | 168 | 204 | 235 | 226 | 142 | 104 | 101 |
| 5 | C s | 24 | 75 | 82 | 125 | 122 | 97 | 80 | 62 |
| | C h | 92 | 172 | 243 | 274 | 262 | 129 | 112 | 100 |
| 10 | C s | 58 | 86 | 102 | 116 | 114 | 94 | 81 | 60 |
| | C h | 85 | 166 | 225 | 252 | 243 | 117 | 108 | 96 |
| 15 | C s | 97 | 97 | 103 | 107 | 102 | 88 | 75 | 53 |
| | C h | 78 | 131 | 174 | 211 | 187 | 109 | 99 | 92 |
| 20 | C s | 75 | 82 | 83 | 92 | 90 | 76 | 58 | 35 |
| | C h | 69 | 123 | 140 | 145 | 138 | 100 | 94 | 90 |
| 30 | C s | 45 | 60 | 62 | 65 | 60 | 45 | 32 | 21 |
| | C h | 65 | 74 | 86 | 102 | 101 | 96 | 87 | 85 |

貯蔵は45°C湿度70%にて250日放置したのち、10Ω連続放電にて容量を調べた。電池Bにおける初期容量を100とし、250日目の容量をB'とする。また電池Aの250日目の容量をA'とする。表2のCs(貯蔵容量)とは $(A' - B') / (100 - B')$ をパーセントであらわしたものである。また2Ω連続放電試験を行つて重負荷特性を調べた。このさい、電池Bの容量をbとし電池Aの容量をaとしたとき、Ch(重負荷比容量)とは $(a - b) / b$ をパーセントであらわしたものである。Cs>0, Ch>100であれば効果ある

ことを示すものである。表2から明らかなように本発明の方法ではビスマスの混合比が1~40重量%、ポリビニールアルコール中のホー酸のモル比が0.3~20%の間でよい効果があらわれていることがわかつた。また同様にして金属ビスマスの代りにタリウム、スズ、カドミウム、鉛、インジウム、アンチモン、テルルなどにつき同様の検討を行なつた結果効果の大小はあるが、これら金属の混合比が40モル%、ポリビニールアルコール中のホー酸のモル比が0.3~20%の範囲内では効果があることが判つた。

実施例 3

実施例1乃至2において亜鉛に混合するビスマスその他金属の代りにそれら金属の酸化物を、金属に換算して同じ重量パーセントになるように均一に混合して同様の試験を行なつたところ、酸化物も金属と同様の効果があることがわかつた。す

なわち、これら金属の酸化物は、金属亜鉛と接触せしめ、アルカリ液が存在すると、たとえば、
 $3 \text{Zn} + \text{M}_2\text{O}_3 \rightarrow 3 \text{ZnO} + 2\text{M}$ のような反応によりそれら金属の多孔体を形成し、いずれも金属集電体として作用することを確認した。